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Explanation of Anomalous Scaling of Swollen Entangled Chains

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ABSTRACT: The unexpected scaling dependence $R_n \sim n^{0.72}$ of the size R_n of the chain section with n monomers observed in recent numerical simulations of a swollen network and globule is explained on the basis of the slip-tube model. We demonstrate that the anomalous exponent 0.72 is the result of a crossover between swollen chain scaling with Flory exponent 0.6 on small length scales and chain stretching with exponent 1 on larger length scales. This picture confirms that swelling of network chains occurs by their disinterpenetration on small length scales.

Topological entanglements of polymers due to chain uncrossability is one of the most interesting problems of polymer physics. These topological interactions play a fundamental role in rheological, dynamic, and elastic properties of entangled polymer solutions, melts, and networks.[1−4] Topological restrictions imposed by neighboring chains significantly restrict motion and deplete a set of accessible conformations of a given chain. It is usually accepted that entanglements affect only conformations of polymer chains on scales larger than entanglement length. Numerous tube models of entanglements are based on this fundamental idea (see refs 5 and 6 and references therein). The main assumption of all these models is that chains are constrained to confining tubes, which restrict polymer conformations only on scales larger than the diameter of these tubes.

Recently this idea was challenged by the interpretation of the results of computer simulations of swollen polymer globules[7,8] (studied at short time scales at which they did not have time to disentangle) and networks.[9] In both cases it was reported that the dependence

$$R_n \sim n^{\nu} \tag{1}$$

of the size R_n of the segment of an entangled chain on the number n of monomers in this segment is characterized by the anomalous exponent $\nu \simeq 0.72$. The fact that this exponent significantly exceeds the Flory exponent $\nu_F \simeq 0.6$ for a chain in a good solvent was interpreted as evidence of a new fractal structure of polymer chains caused by topological interactions.

This interpretation was justified by a Flory-like argument based on the assumption that polymer chains do not disinterpretate upon swelling. Consider a chain segment consisting of n monomers in a melt of linear chains in d-dimensional space. Since chains in a melt are ideal, the size of this segment is proportional to $bn^{1/2}$. The volume pervaded by the segment is $b^d n^{d/2}$ and contains $n^{d/2}$ monomers of $n^{d/2-1}$ similar segments, where b is the monomer size. If all these segments are assumed to swell to the size R_n but not disinterpenetrate, the Flory free energy of this group of $n^{d/2-1}$ segments can be written as

$$F \simeq kT\left[n^{d/2-1}\frac{{R_n}^2}{b^2 n} + b^d\frac{(n^{d/2})^2}{{R_n}^d}\right] \tag{2}$$

where b^d is the monomeric excluded volume, k is the Boltzmann constant, and T is the absolute temperature. The minimum of this free energy corresponds to the size of a swollen segment $R_n \approx bN^{\nu}$ where the scaling exponent is

$$\nu = \frac{d+4}{2d+4} \tag{3}$$

This expression was derived by Putz et al.[9] and generalized by Sukumaran et al.,[10] and for 3-dimensional space it leads to $\nu = 0.7$. Putz et al.[9] and Lee et al.[7] suggest that this argument can be used on all length scales from the monomer size up to the entanglement length, and on these length scales polymer is a fractal with the fractal dimension $1/\nu = 10/7$. The assumption of no disinterpenetration implies that all neighboring chains are glued together by entanglements on small length scales all the way down to the monomer size b. This result is in striking disagreement with the main assumption of tube models that chains are not constrained on length scales less than the tube diameter and chain conformations are not affected by entanglements on such small length scales. In the present paper we provide an alternative explanation of the results of computer simulations of swollen polymer networks[9] and globules[7] on the basis of the slip-tube model of polymer networks.[6,11,12]

To describe chain conformations in deformed networks, one has to introduce affine length scale R_{aff}. Chain deformation on length scales larger than affine is proportional to macroscopic deformation of the whole network. Chains conformations on length scales smaller than affine are those of stretched segments of affine size and are not affected by topological constraints.[13] In a swollen network there is an additional length scale, called correlation length ξ, characterizing the concentration fluctuations.[1,3] On length scales smaller than the correlation length, monomers are surrounded by solvent and other monomers of the same chain segment. Therefore, the size R_n of chain segments containing n mono-

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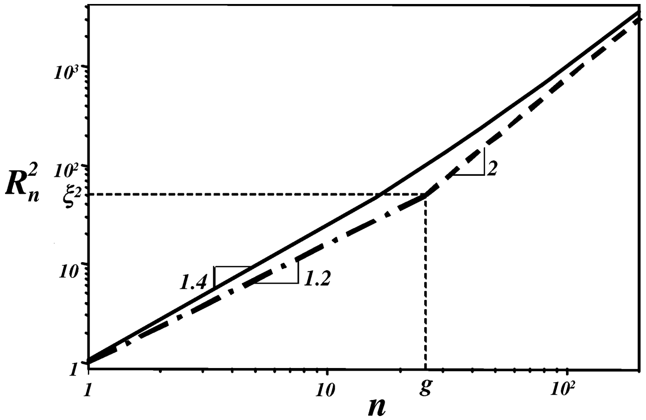

Figure 1. Dependence of the square of the size R_n^2 of chain sections on the number of monomers n in these sections (for $g = 25$ and $b = 1$).

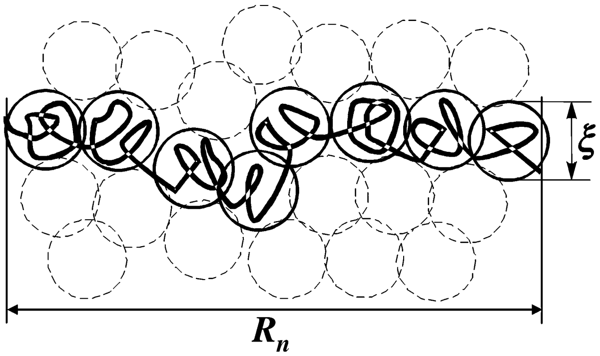

Figure 2. Chain section in a network swollen to equilibrium is a stretched array of concentration blobs.

mers smaller than correlation length is the same as in dilute solutions

$$R_n \sim n^{\nu_F} \tag{4}$$

with $\nu_F = 0.6$ in a good solvent (see dash−dotted line for R_n^2 in Figure 1).

The network swells until equilibrium is reached with the osmotic pressure balanced by the tension in stretched network strands.[3] Each elastically effective network strand is pulled at its ends (cross-links) by the neighboring strands into a stretched state (array of tension blobs[3]). In a network swollen to equilibrium, cost for stretching network strands (kT per tension blob) is balanced by osmotic gain (kT per concentration blob), making the size of tension and concentration blobs, ξ, proportional to each other. Therefore, conformations of an affine strand can be described as a stretched array of concentration blobs of the size ξ with g monomers ($\xi \sim g^{\nu_F}$); see Figure 2. The size R_n of an n-mer larger than the concentration blob, but smaller than the affine strand, is therefore

$$R_n \simeq \xi \frac{n}{g} \tag{5}$$

This dependence for the square size R_n^2 of these sections is shown as a dashed line in Figure 1. The crossover between the swollen chain regime on a smaller length scale (eq 4) and the stretched chain regime on a larger length scale (eq 5) can be approximated by

$$R_n^2 \simeq b^2 n^{2\nu_F} + \left(\xi \frac{n}{g}\right)^2 \tag{6}$$

and is depicted by the solid line in Figure 1. This solid line is well approximated by a power law with an intermediate exponent for small values of n. Thus, the origin of the pseudo-scaling dependence observed in the computer simulations can be explained as a crossover between two simple scaling behaviors and is expected even for unentangled networks.

Below we present a quantitative comparison between the results of simulations and the predictions of the slip-tube model. This model was developed for the description of entangled polymer networks, but it can also be applied to deformed polymer globules on time scales shorter than the Rouse time of the chain so that there are no chain retractions inside the tube. This condition is satisfied in the simulations of a polymer globule described in ref 7.

In general, the mean-square size of a chain section containing n monomers can be written as

$$\langle R_n^2 \rangle = \langle R_n \rangle^2 + \langle \delta R_n^2 \rangle \tag{7}$$

where $\langle R_n \rangle$ is the average size of the section due to stretching and $\delta R_n = R_n - \langle R_n \rangle$ is the deviation of the section size from its average value. We will demonstrate below that the combined effect of these two terms (eq 7) leads to approximate scaling of the mean-square size of the section $\langle R_n^2 \rangle \sim n^{2\nu}$ with the effective exponent $\nu \simeq 0.72$ intermediate between $\nu_F = 0.6$ due to fluctuations and 1 due to stretching.

Consider a section of the chain, called affine strand, consisting of N_{aff} monomers, with the size in the deformed state equal to the affine length R_{aff}. Affine length can be determined from the condition that the amplitude of fluctuations of the affine strand is equal to the distance between entanglements.[13] Chain sections with size smaller than the network strand or globular size are ideal in the undeformed state, and therefore the size of the strand containing N_{aff} monomers is equal to $bN_{aff}^{1/2}$. As polymer swells with its linear dimension increasing by the factor λ, the size of the strand with N_{aff} monomers increases by the same factor and is equal to

$$R_{aff} \simeq \lambda b N_{aff}^{1/2} \tag{8}$$

Conformations of the affine strand in the deformed state[13] are those of a chain stretched by its ends by the factor λ. Therefore, the average size of a chain section smaller than the affine strand is proportional to the number n of its monomers:

$$\langle R_n \rangle \simeq R_{aff} \frac{n}{N_{aff}} = \lambda b \frac{n}{N_{aff}^{1/2}} \tag{9}$$

The average distance between entanglements is the average size of an entanglement strand containing N_e monomers and therefore it is equal to

$$a \simeq \lambda b \frac{N_e}{N_{aff}^{1/2}} \tag{10}$$

To find N_{aff} consider chain conformations on scales smaller than R_{aff}. A section of a chain with n monomers in a good solvent can be represented as a Gaussian chain with n/g effective monomers (blobs) of the size ξ, each consisting of g monomers. The size of these blobs increases with decreasing polymer volume fraction ϕ in an athermal solvent as

$$\xi \simeq b\phi^{-3/4} \tag{11}$$

Polymer volume fraction ϕ is related to the monomer number density $c = \phi/b^3$. Note that the polymer volume fraction is related to the deformation factor as $\phi = \lambda^{-3}$. The number of monomers in a correlation blob is equal to

$$g = \left(\frac{\xi}{b}\right)^{5/3} \simeq \phi^{-5/4} \tag{12}$$

The mean-square fluctuations of a Gaussian chain are unaffected by its deformation and for any strand longer than the correlation strand ($n > g$) can be estimated as the size of the free chain in an athermal solvent at the same volume fraction ϕ

$$\langle \delta R_n^{\,2} \rangle \simeq \xi^2 \frac{n}{g} = b^2 n \phi^{-1/4} \quad \text{for } n > g = \phi^{-5/4} \tag{13}$$

Mean-square fluctuations of a chain section shorter than the correlation blob are the same as for a free chain in a dilute athermal solution

$$\langle \delta R_n^{\,2} \rangle \simeq b^2 n^{6/5} \quad \text{for } n < g = \phi^{-5/4} \tag{14}$$

The mean-square fluctuations of an affine strand are equal to (see eq 13 for $n = N_{\mathrm{aff}}$)

$$\langle \delta R_{\mathrm{aff}}^{\,2} \rangle \simeq b^2 N_{\mathrm{aff}} \phi^{-1/4} \tag{15}$$

Since fluctuations of the affine strand are constrained by entanglements, we can find its size by equating the square of the tube diameter (eq 10) to mean-square fluctuations of the affine strand (eq 15), $a^2 \simeq \langle \delta R_{\mathrm{aff}}^{\,2} \rangle$. From this equation we find the number of monomers in the affine strand

$$N_{\mathrm{aff}} \simeq \lambda N_{\mathrm{e}} \phi^{1/8} \tag{16}$$

Fluctuations of the size of chain sections larger than affine (with number of monomers $n > N_{\mathrm{aff}}$) are determined by tube length fluctuations of these sections (breathing modes),[2,3] and their mean-square amplitude is given by

$$\langle \delta R_n^{\,2} \rangle \simeq a^2 (N/N_{\mathrm{aff}})^{1/2} \simeq \lambda^{1/2} b^2 N_{\mathrm{e}}^{\,1/2} \phi^{-3/16} N^{1/2} \quad \text{for } n > N_{\mathrm{aff}} \tag{17}$$

The three limiting expressions for mean-square fluctuations of the size of a chain section, $\langle \delta R_n^{\,2} \rangle$ (eqs 13, 14, and 17), can be combined in a single crossover expression

$$\langle \delta R_n^{\,2} \rangle = b^2 N_{\mathrm{e}} \lambda m^{1/10} \left(1 + \frac{n m^{1/10}}{N_{\mathrm{e}} \lambda}\right)^{1/2} \left[1 - \exp\left(-\frac{n m^{1/10}}{N_{\mathrm{e}} \lambda}\right)\right] \tag{18}$$

where m is the smallest of the number of monomers in the segment, n, or in the blob, g

$$m = \min(n, g) = \min\,(n, \phi^{-5/4}) \tag{19}$$

The average size of the segment with n monomers (eq 9) is valid only for intermediate segment length $g < n < N_{\mathrm{aff}}$. Longer segments deform affinely from their undeformed size $bn^{1/2}$

$$\langle R_n \rangle = \lambda b n^{1/2} \quad \text{for } n > N_{\mathrm{aff}} \tag{20}$$

Both expressions 9 and 20 are valid for large deformations $\lambda \gg 1$. The full expression valid for all values of λ and n was reported in ref 12.

$$\langle R_n \rangle^2 = b^2 N_{\mathrm{e}} \lambda g^{1/10} \left\{ \frac{\lambda^2}{g^{1/5}} \left(\frac{n}{N_{\mathrm{aff}}} - 1 + \mathrm{e}^{-n/N_{\mathrm{aff}}} \right) + \frac{1}{2} \left(\frac{\lambda^2}{g^{1/5}} - 1 \right) \left[\left(1 + \frac{n}{N_{\mathrm{aff}}} \right) \mathrm{e}^{-n/N_{\mathrm{aff}}} - 1 \right] \right\} \tag{21}$$

where $g \approx \phi^{-5/4}$ is the number of monomers in the concentration blob (eq 12) and N_{aff} is defined in eq 16. This expression is valid for a polymer chain with size much larger than the affine length.

Below we compare the results of computer simulations[7] for the mean-square size of the section containing n monomers with the predictions for $\langle R_n^{\,2} \rangle$ (eq 7) of the slip-tube model with fluctuations part $\langle \delta R_n^{\,2} \rangle$ given by eq 18 and the square of the average distance $\langle R_n \rangle^2$ presented in eq 21. We concentrate on the quantitative analysis of the swollen globule[7] rather than swollen networks[9] because the globule contains linear chain sections much larger than the entanglement strand.

The chain simulated in ref 7 had a very large degree of polymerization $N = 50\,000$ but collapsed into a relatively small globule with dry radius $R = 22.4\sigma$, where σ is the size of a Lennard-Jones monomer. The segments of this chain containing more than $n_{\max} \approx (R/b)^2$ monomers of size $b \approx \sigma$ with end-to-end distance in a coil state larger than the globular size R do not fit inside the globule and are reflected back from its surface. Therefore, the size of long chain sections in the globule is limited by the globular dimension. This effect can be taken into account by replacing the actual number of monomers in a long chain section with $n \gg n_{\max}$ by its limiting value $n_{\max}$. Short sections of the chain with $n \ll n_{\max}$ are much smaller than the globular size, and their conformations are not affected by its boundaries. We use the simple interpolation formula that replaces the number of monomers n in a chain section by the effective number $\hat{n}$

$$n \rightarrow \hat{n} = \frac{n}{1 + n/n_{\max}} \tag{22}$$

From the comparison of our theory with simulation data for the dry globule, we estimate $n_{\max} \simeq 700$, and therefore the simulated polymer consists of 70 such sections of $n_{\max}$ monomers.

One of the most important parameters characterizing topological interactions is the degree of polymerization between entanglements, N_{e}. Unfortunately, this parameter is not uniquely defined, and its exact numerical value depends both on the measured quantity and on the theoretical model. For example, degree of polymerization between entanglements can be extracted from the shear modulus

$$G_{\mathrm{e}} = AkT \frac{c}{N_{\mathrm{e}}} \tag{23}$$

where c is the monomer number density and A is the model-dependent numerical constant. This constant is

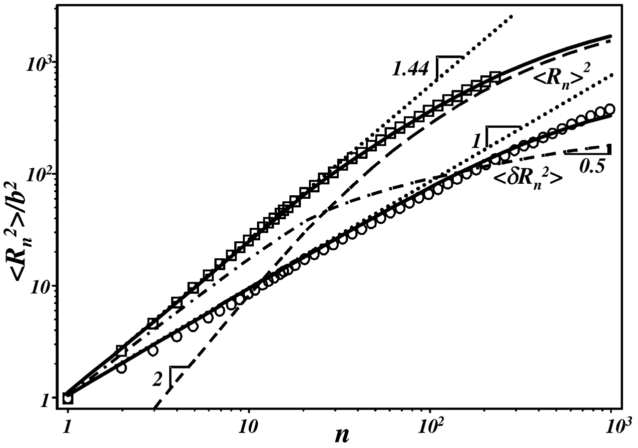

Figure 3. Log–log plot of the mean-square end-to-end distance $\langle R_n^2\rangle$ of segments with n monomers in the dry (○) and swollen (□) globule.[7] Solid lines are the corresponding predictions of $\langle R_n^2\rangle$ by the slip-tube model. Lower straight dotted line represents the mean-square size $\langle R_n^2\rangle = b^2n$ of these segments in the undeformed ideal state. Dashed line shows the contribution of the square of the average end-to-end distance $\langle R_n\rangle^2$ of swollen chain segments. Dash–doted line depicts the contribution of the mean-square fluctuations of the end-to-end distance $\langle\delta R_n^2\rangle$ of swollen chain segments. Upper straight dotted line has the slope $2\nu = 1.44$.

often taken to be unity, $A = 1$, in the analysis of experimental results.[3] In the Doi–Edwards tube model of a polymer melt the factor A is equal to $4/5$.[2] In the slip-tube model this constant is equal to $2/7$.[6] Lee et al. estimate the number of entanglements in their globule to be of order of 30.[7] This corresponds to $N_e \simeq (2/7) \times 30 \simeq 10$ in our slip-tube model.

Figure 3 presents the comparison of the mean-square size $\langle R_n^2\rangle$ of the chain section with n monomers obtained in computer simulations[7] and predicted by the slip-tube theory. Circles represent mean-square end-to-end distance of chain sections in the dry globule. Lower straight dotted line shows the mean-square size $\langle R_n^2\rangle = b^2n$ of these segments in the undeformed Gaussian state. Deviations between circles and the dashed line are due to the finite size of the globule and reflections of the chain from the globular boundary. Lower solid line is the theoretical estimate of $\langle R_n^2\rangle$ taking into account the finite size of the globule using the approximate crossover eq 22

$$\langle R_n^2\rangle = b^2\hat{n} = \frac{b^2n}{1 + n/n_{\max}} \qquad (24)$$

with $n_{\max} = 700$. The agreement between the simulation results and the theory is quite reasonable in light of the simplicity of this approximation.

Squares in Figure 3 represent simulation results for the mean-square end-to-end distance of chain sections in the swollen globule. The deformation factor λ can be estimated as the ratio of sizes of the longest reported strand in the swollen and dry globule. This strand with $n \simeq 220$ is larger than the affine stand and therefore deforms affinely. This analysis yields the deformation factor $\lambda \simeq 2.3$. The upper solid line represents the prediction of $\langle R_n^2\rangle$ by the slip-tube model for the values of parameters $N_e = 10$, $n_{\max} = 700$, and $\lambda = 2.3$.

For shorter chain sections with $2 < n < 50$, both theory and numerical simulations demonstrate a power law dependence $\langle R_n^2\rangle \sim n^{2\nu}$ with effective exponents $\nu = 0.72$ both for numerical data and for theoretical results (indicated by the upper straight dotted line). The power law dependence of theoretical predictions with intermediate exponent $\nu \simeq 0.72$ is due to the crossover between two contributions to $\langle R_n^2\rangle$ (eq 7). The first contribution (depicted by the dash–dotted line) is due to mean-square fluctuations of the end-to-end distance $\langle\delta R_n^2\rangle$ of swollen chain segments (eq 18). The initial slope of this contribution is equal to $2\nu_F = 1.2$, where ν_F is the Flory exponent of swollen linear polymers. The second contribution to $\langle R_n^2\rangle$ (shown by the dashed line) is the square of the average end-to-end distance $\langle R_n\rangle^2$ of the swollen chain segments (eq 21). The initial slope of this line for small values of n is equal to 2. Note that the value of the effective exponent ν (eq 1) is not universal but depends on the set of parameters such as the degree of swelling, λ, and the degree of polymerization between entanglements, N_e. For example, the effective exponent of swollen bimodal network of 100-mers with mole fraction 0.16 and 5-mers with mole fraction 0.84 is $\nu = 0.62$, which is much closer to the Flory exponent of swollen linear polymers $\nu_F = 0.6$.[14]

We conclude that the slip-tube model predicts the main features of swollen entangled polymer globules and networks. This observation supports the main result of this model that entanglement tube deforms nonaffinely and chains disinterpenetrate upon swelling on scales up to affine length, as was observed in the simulations of Sommer and Lay.[14]

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